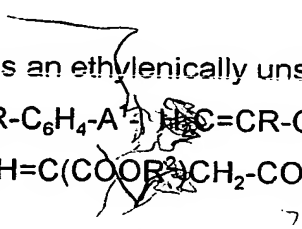
CLAIMS

1. A composition comprising a solvent and a block copolymer, in which the block copolymer comprises a hydrophilic core block and at least two terminal blocks, each terminal block being stimulus-responsive in which the blocks are each formed at least in part by the polymerisation of ethylenically unsaturated monomers, wherein the average degree of each terminal block is at least 20 characterised in that the core block comprises zwitterionic pendant groups, and has a degree of polymerisation of at least 100.

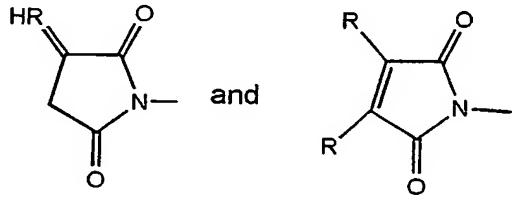
2. A composition according to claim 1 which has an A-B-A structure, the B block being the core block and the A blocks being the terminal blocks.

3. A composition according to claim 1 or claim 2 in which the monomers from which the core block is formed comprise compounds of the general formula I



Y B X I

in which Y is an ethylenically unsaturated group selected from H_2C=CR-CO-A-, H_2C=CR-C_6H_4-A^1-, H_2C=CR-CH_2A^2, R^2O-CO-CR=CR-CO-O, RCH=CH-CO-O-, RCH=C(COOR^2)CH_2-CO-O,



and

A is -O- or NR^1;

A^1 is selected from a bond, $(CH_2)_l A^2$ and $(CH_2)_l SO_3$- in which l is 1 to 12;

A^2 is selected from a bond, -O-, O-CO-, CO-O, CO-NR^1-, -NR^1-CO, O-CO-NR^1-, NR^1-CO-O-;

R is hydrogen or C_{1-4} alkyl;

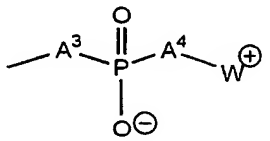
R^1 is hydrogen, C_{1-4} alkyl or BX;

R^2 is hydrogen or C_{1-4} alkyl;

B is a bond, or a straight branched alkanediyl, alkylene oxaalkylene, or alkylene (oligooxalkylene) group, optionally containing one or more fluorine substituents;

X is a zwitterionic group.

4. A composition according to claim 3 in which X is a group of the general formula II



II

in which the moieties A^3 and A^4, which are the same or different, are -O-, -S-, -NH- or a valence bond, preferably -O-, and W^+ is a group comprising an ammonium, phosphonium or sulphonium cationic group and a group linking the anionic and cationic moieties which is preferably a C_{1-12}-alkanediyl group,

preferably in which W^+ is a group of formula $-W^1-N^+R^3_3$, $-W^1-P^+R^4_3$, $-W^1-S^+R^4_2$ or $-W^1$-Het$^+$ in which:

W^1 is alkanediyl of 1 or more, preferably 2-6 carbon atoms optionally containing one or more ethylenically unsaturated double or triple bonds, disubstituted-aryl (arylene), alkylene arylene, arylene alkylene, or alkylene aryl alkylene, cycloalkanediyl, alkylene cycloalkyl, cycloalkyl alkylene or alkylene cycloalkyl alkylene, which group W^1 optionally contains one or more fluorine substituents and/or one or more functional groups; and

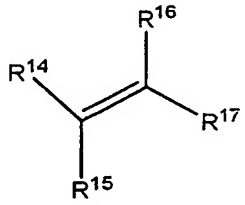
either the groups R^3 are the same or different and each is hydrogen or alkyl of 1 to 4 carbon atoms, preferably methyl, or aryl, such as phenyl, or two of the groups R^3 together with the nitrogen atom to which they are attached form an aliphatic heterocyclic ring containing from 5 to 7 atoms, or the three groups R^3 together with the nitrogen atom to which they are attached as heteroaromatic ring having 5 to 7 atoms, either of which rings

may be fused with another saturated or unsaturated ring to form a fused ring structure containing from 5 to 7 atoms in each ring, and optionally one or more of the groups R^3 is substituted by a hydrophilic functional group, and

the groups R^4 are the same or different and each is R^3 or a group OR^3, where R^3 is as defined above; or

Het is an aromatic nitrogen-, phosphorus- or sulphur-, preferably nitrogen-, containing ring, for example pyridine.

5. A composition according to any preceding claim in which the monomers from which the terminal blocks are formed comprise compounds of the formula VI



VI

where R^{14} is selected from the group consisting of hydrogen, halogen, C_{1-4} alkyl and groups $COOR^{18}$ in which R^{18} is selected from the group consisting of hydrogen and C_{1-4} alkyl;

R^{15} is selected from the group consisting of hydrogen, halogen and C_{41-} alkyl;

R^{16} is selected from the group consisting of hydrogen, halogen, C_{1-4} alkyl and groups $COOR^{18}$ provided that R^{14} and R^{16} are not both $COOR^{18}$

or R^{14} and R^{16} may together form $CONR^{19}CO$ in which R^{19} is a C_{1-20} alkyl group; and

R^{17} is selected from the group consisting of C_{1-10} alkyl, C_{1-20} alkoxycarbonyl, mono- and di- (C_{1-20} alkyl) amino carbonyl, C_{6-20} aryl, C_{7-20} aralkyl, C_{6-20} aryloxy carbonyl, C_{7-20} aralkoxyl carbonyl, C_{6-20} arylamino carbonyl, C_{7-20} aralkyl amino carbonyl, C_{2-20} aralkylamino and C_{2-10} acyloxy groups, in which an alkyl or aryl group has a substituent which is responsive to a stimulus and in which any of the alkyl or aryl groups may additionally be substituted by one or more substituents selected from halogen atoms,

alkoxy, oligo-alkoxy, aryloxy, acyloxy, acylamino, amine (including mono and di-alkyl amino and trialkylammonium in which the alkyl groups may be substituted), carboxyl, sulphonyl, phosphoryl, phosphino, (including mono- and di- alkyl phosphine and tri-alkylphosphonium), zwitterionic, hydroxyl groups, vinyloxycarbonyl and other vinylic or allylic substituents, and reactive silyl or silyloxy groups, such as trialkoxysilyl groups.

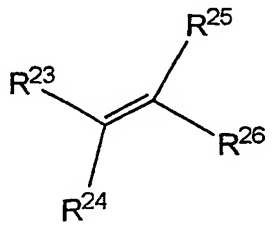
6. A composition according to claim 5 in which the stimulus responsive substituent is a proton donor or proton acceptor.

7. A composition according to claim 6 in which the stimulus responsive substituent comprises a group selected from carboxylic, carboxylate, SO_3H, SO_3^-, PO_3HR^{20} and $PO_2^-R^{20}$ and PO_3^{2-}, in which R^{20} selected from the group consisting of hydroxyl, C_{1-12} alkyl C_{1-12} alkoxy, C_{6-18} aryl, C_{6-18} aryloxy, C_{7-18} aralkyl and C_{7-18} aralkoxy.

8. A composition according to claim 6 in which the stimulus responsive substituent is selected from the group consisting of NR^{21}_2, $N^+R^{21}_2H$, PR^{22}_2, $P^+R^{22}_2H$, SR^{21}, $S^+R^{21}H$, wherein the or each group R^{21} is selected from the group consisting of hydrogen, optionally substituted C_{1-20} alkyl and aryl, or the two groups R^{21} are joined to form, together with the heteroatom to which they are each attached, a 5-7 membered heterocycle, and each R^{22} is R^{21} or OR^{21}.

9. A composition according to claim 8 in which the compound of the formula VII is ω-(N,N-dialkylamino)alkyl-(alk)acrylate or -(alk)acrylamide, preferably 2-(diisopropyl amino) ethyl methacrylate.

10. A composition according to any preceding claim in which the monomers from which each terminal block and/or the core block is formed comprise comonomers, selected from compounds of the general formula VII



VII

in which R^{23} is selected from the group consisting of hydrogen, halogen, C_{1-4} alkyl and groups $COOR^{27}$ in which R^{27} is hydrogen and C_{1-4} alkyl;

R^{24} is selected from the group consisting of hydrogen, halogen and C_{1-4} alkyl;

R^{25} is selected from the group consisting of hydrogen, halogen, C_{1-4} alkyl and groups $COOR^{27}$ provided that R^{23} and R^{25} are not both $COOR^{27}$; and

R^{26} is selected from the group consisting of C_{1-10} alkyl, C_{1-20} alkoxycarbonyl, mono- and di-(C_{1-20} alkyl) amino carbonyl, C_{6-20} aryl (including alkaryl), C_{7-20} aralkyl, C_{6-20} aryloxycarbonyl, C_{7-20} - aralkyloxycarbonyl, C_{6-20} arylamino carbonyl, C_{7-20} aralkyl-amino carbonyl, hydroxyl and carboxylic C_{2-10} acyloxy groups, any of which may have one or more substituents selected from the group consisting of halogen atoms, alkoxy, oligo-alkoxy, aryloxy, acyloxy, acylamino, amine (including mono and di-alkyl amino and trialkylammonium in which the alkyl groups may be substituted), carboxyl, sulphonyl, phosphoryl, phosphino, (including mono- and di- alkyl phosphine and tri-alkylphosphonium), zwitterionic, hydroxyl, vinyloxycarbonyl and other vinylic and allylic groups, and reactive silyl and silyloxy groups, such as trialkoxysilyl groups;

or R^{26} and R^{25} or R^{25} and R^{23} may together form $-CONR^{28}CO$ in which R^{28} is a C_{1-20} alkyl group.

11. A composition according to any preceding claim in which the mean degree of polymerisation of the core block is in the range 100 to 10,000.

12. A composition according to any preceding claim in which the polydispersity of block weight of the core block is in the range 1.1 to 2.0.

13. A composition according to any preceding claim in which the mean degree of polymerisation of the terminal blocks is in the range 30 to 100, preferably 50 to 80.

14. A composition according to any preceding claim in which the polydispersity of block weight of the terminal blocks is in the range 1.1 to 3.0.

15. A composition according to any preceding claim in which the ratio of the mean degree of polymerisation of the core block to the mean degree of polymerisation of each of the terminal blocks is in the range 20:1 to 1:1, preferably in the range 10:1 to 2:1.

16. A composition according to any preceding claim in which the solvent is aqueous.

17. A composition according to claim 6 in which the said substituent is a proton acceptor having a pH more than the pK_A of the conjugate acid of the said substituent.

18. A composition according to claim 6 in which the said substituent is a proton acceptor, having a pH less than the pK_A of the conjugate acid of the said substituent.

19. A composition according to claim 6 in which the said substituent is a proton donor having a pH more than the pK_A of the said substituent.

20. A composition according to claim 6 in which the said substituent is a proton donor, having a pH less than the pK_A of the said substituent.

21. A composition according to any preceding claim which is a gel.

22. A composition according to any preceding claims 1 to 20 which is a liquid.

23. A composition according to any preceding claim which comprises a biologically active agent, preferably a pharmaceutically or diagnostically active agent.

24. A composition according to any preceding claim which comprises an imaging agent, preferably selected from the group consisting of visible light dyes, UV dyes, radiopaque agents, nmr imaging agents and radioactive agents.

25. A method in which a composition according to any claim is subjected to a stimulus to which the stimulus-responsive blocks respond, whereby the terminal blocks respond to the stimulus to change the

mechanical characteristics of the composition.

26. A method according to claim 25 in which the stimulus is subsequently removed, whereupon the mechanical characteristics of the composition revert at least in part to their original values.

27. A method according to claim 25 or 26 in which the stimulus is a change in the pH.

28. A method according to claim 25 or 26 in which the stimulus is selected from the group consisting of temperature change, shear, change in dissolved ion concentration and electromagnetic irradiation.

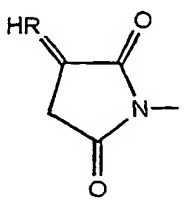
29. A polymerisation process in which core block ethylenically unsaturated monomers comprising a zwitterionic monomer are polymerised to form a core block having average degree of polymerisation of at least 100 initiation sites are formed at at least two locations on the core block and terminal block ethylenically unsaturated monomers are polymerised from the initiation sites on the core block to form at least two terminal blocks having an average degree of polymerisation of at least 20, wherein the terminal block ethylenically unsaturated monomers comprise monomers having stimulus responsive pendant groups.

30. A polymerisation process according to claim 29 in which initiation sites are formed at each end of the block and not elsewhere on the core block whereby an A-B-A block copolymer is formed.

31. A polymerisation process according to claim 29 or 30 in which the core block ethylenically unsaturated monomers comprise compounds of the general formula I

Y B X I

in which Y is an ethylenically unsaturated group selected from H_2C=CR-CO-A-, H_2C=CR-C_6H_4-A^1-, H_2C=CR-CH_2A^2, R^2O-CO-CR=CR-CO-O, RCH=CH-CO-O-, RCH=C(COOR^2)CH_2-CO-O,



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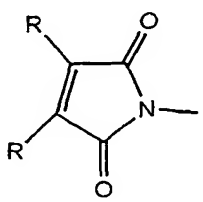


A is -O- or NR^1;

A^1 is selected from a bond, $(CH_2)_lA^2$ and $(CH_2)_l SO_3$- in which l is 1 to 12;

A^2 is selected from a bond, -O-, O-CO-, CO-O, $CO-NR^1$-, $-NR^1-CO$, $O-CO-NR^1$-, NR^1-CO-O-;

R is hydrogen or C_{1-4} alkyl;

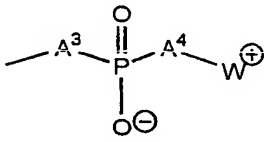
R^1 is hydrogen, C_{1-4} alkyl or BX;

R^2 is hydrogen or C_{1-4} alkyl;

B is a bond, or a straight branched alkanediyl, alkylene oxaalkylene, or alkylene (oligooxalkylene) group, optionally containing one or more fluorine substituents; and

X is a zwitterionic group.

32. A polymerisation process according to claim 31 in which X is a group of the general formula II



II

in which the moieties A^3 and A^4, which are the same or different, are -O-, -S-, -NH- or a valence bond, preferably -O-, and W^+ is a group comprising an ammonium, phosphonium or sulphonium cationic group and a group linking the anionic and cationic moieties which is preferably a C_{1-12}-alkanediyl group,

preferably in which W^+ is a group of formula $-W^1-N^+R^3_3$, $-W^1-P^+R^4_3$, $-W^1-S^+R^4_2$ or $-W^1$-Het$^+$ in which:

W^1 is alkanediyl of 1 or more, preferably 2-6 carbon atoms optionally containing one or more ethylenically unsaturated double or triple bonds, disubstituted-aryl (arylene), alkylene arylene, arylene alkylene, or alkylene aryl alkylene, cycloalkanediyl, alkylene cycloalkyl, cycloalkyl alkylene or

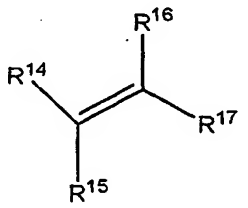
alkylene cycloalkyl alkylene, which group W^1 optionally contains one or more fluorine substituents and/or one or more functional groups; and

either the groups R^3 are the same or different and each is hydrogen or alkyl of 1 to 4 carbon atoms, preferably methyl, or aryl, such as phenyl, or two of the groups R^3 together with the nitrogen atom to which they are attached form an aliphatic heterocyclic ring containing from 5 to 7 atoms, or the three groups R^3 together with the nitrogen atom to which they are attached as heteroaromatic ring having 5 to 7 atoms, either of which rings may be fused with another saturated or unsaturated ring to form a fused ring structure containing from 5 to 7 atoms in each ring, and optionally one or more of the groups R^3 is substituted by a hydrophilic functional group, and

the groups R^4 are the same or different and each is R^3 or a group OR^3, where R^3 is as defined above; or

Het is an aromatic nitrogen-, phosphorus- or sulphur-, preferably nitrogen-, containing ring, for example pyridine.

33. A polymerisation process according to any of claims 29 to 32 in which the terminal block ethylenically unsaturated monomers comprise compounds of the formula VI



VI

where R^{14} is selected from the group consisting of hydrogen, halogen, C_{1-4} alkyl and groups $COOR^{18}$ in which R^{18} is selected from the group consisting of hydrogen and C_{1-4} alkyl;

R^{15} is selected from the group consisting of hydrogen, halogen and C_{41-} alkyl;

R^{16} is selected from the group consisting of hydrogen, halogen, C_{1-4} alkyl and groups $COOR^{18}$ provided that R^{14} and R^{16} are not both $COOR^{18}$

or R^{14} and R^{16} may together form $CONR^{19}CO$ in which R^{19} is a C_{1-20}

alkyl group; and

R^{17} is selected from the group consisting of C_{1-10} alkyl, C_{1-20} alkoxycarbonyl, mono- and di- (C_{1-20} alkyl) amino carbonyl, C_{6-20} aryl, C_{7-20} aralkyl, C_{6-20} aryloxy carbonyl, C_{7-20} aralkoxyl carbonyl, C_{6-20} arylamino carbonyl, C_{7-20} aralkyl amino carbonyl, C_{2-20} aralkylamino and C_{2-10} acyloxy groups, in which an alkyl or aryl group has a substituent which is responsive to a stimulus and in which any of the alkyl or aryl groups may additionally be substituted by one or more substituents selected from halogen atoms, alkoxy, oligo-alkoxy, aryloxy, acyloxy, acylamino, amine (including mono and di-alkyl amino and trialkylammonium in which the alkyl groups may be substituted), carboxyl, sulphonyl, phosphoryl, phosphino, (including mono- and di- alkyl phosphine and tri-alkylphosphonium), zwitterionic, hydroxyl groups, vinyloxycarbonyl and other vinylic or allylic substituents, and reactive silyl or silyloxy groups, such as trialkoxysilyl groups.

34. A polymerisation process according to claim 33 in which the stimulus responsive substituent comprises a group selected from carboxylic, carboxylate, SO_3H, SO_3^-, PO_3HR^{20} and $PO_2^-R^{20}$ and PO_3^{2-}, in which R^{20} is selected from the group consisting of hydroxyl, C_{1-12} alkyl C_{1-12} alkoxy, C_{6-18} aryl, C_{6-18} aryloxy, C_{7-18} aralkyl and C_{7-18} aralkoxy.

35. A polymerisation process according to claim 34 in which the stimulus responsive substituent is selected from the group consisting of NR^{21}_2, $N^+R^{21}_2H$, PR^{22}_2, $P^+R^{22}_2H$, SR^{21}, $S^+R^{21}H$, wherein the or each group R^{21} is selected from the group consisting of hydrogen, optionally substituted C_{1-20} alkyl and aryl, or the two groups R^{21} are joined to form, together with the heteroatom to which they are each attached, a 5-7 membered heterocycle, and each R^{22} is R^{21} or OR^{21}.

36. A polymerisation process according to any of claims 29 to 35 in which the polydispersity of the molecular weight of the core block is less than 2.0, preferably in the range 1.1-1.5.

37. A polymerisation process according to any of claims 29 to 36 in which the ratio of the mean degree of polymerisation of the core block to the

mean degree of polymerisation of the terminal blocks is in the range 20:1 to 1:1, preferably in the range 10:1 to 2:1.

38. A polymerisation process according to any of claims 29 to 37 in which each polymerisation step is conducted by controlled radical polymerisation, preferably by atom transfer radical polymerisation.

39. A polymerisation process according to claim 38 in which the core block monomers are polymerised in the presence of a difunctional initiator of the general formula VIII

$$R^{29}R^{30}R^{31}C\text{-}X^{2} \qquad \text{VIII}$$

where:

X^2 is selected from the group consisting of Cl, Br, I, OR^{32}, SR^{33}, SeR^{33}, $OP(=O)R^{33}$, $OP(=O)(OR^{33})_2$, $O\text{-}N(R^{33})_2$ and $S\text{-}C(=S)N(R^{33})_2$, where R^{32} is alkyl of from 1 to 20 carbon atoms in which each of the hydrogen atoms may be independently replaced by halide, R^{33} is aryl or a straight or branched C_1-C_{20} alkyl group, and where an $N(R^{33})_2$ group is present, the two R^{33} groups may be joined to form a 5- or 6-membered heterocyclic ring;

R^{29} is a $C_{1\text{-}6}$ alkyl substituted with $CR^{30}R^{31}X^2$, $X^2R^{31}R^{30}\text{-}C\text{-}C_{1\text{-}4}$ alkoxy- and $X^2R^{31}R^{30}C$- oligo ($C_{1\text{-}4}$ alkoxy);

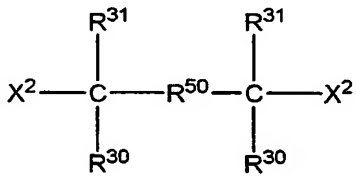
R^{30} and R^{31} are each independently selected from the group consisting of H, halogen, C_1-C_{20} alkyl, C_3-C_8 cycloalkyl, $C(=O)R^{34}$, $C(=O)NR^{35}R^{36}$, COCl, OH, CN, C_2-C_{20} alkenyl, C_2-C_{20} alkenyl oxiranyl, glycidyl, aryl, heterocyclyl, aralkyl, aralkenyl, C_1-C_6 alkyl in which from 1 to all of the hydrogen atoms are replaced with halogen, C_1-C_6 alkyl substituted with from 1 to 3 substituents selected from the group consisting of C_1-C_4 alkoxy, aryl, heterocyclyl, $C(=O)R^{34}$, $C(=O)NR^{35}R^{36}$, $-CR^{30}R^{31}X^2$, oxiranyl and glycidyl;

where R^{34} is alkyl of from 1 to 20 carbon atoms, alkoxy of from 1 to 20 carbon atoms, oligo(alkoxy) in which each alkoxy group has 1 to 3 carbon atoms, aryloxy or heterocyclyloxy any of which groups may have substituents selected from optionally substituted alkoxy, oligoalkoxy, amino (including

mono- and di-alkyl amino and trialkyl ammonium, which alkyl groups, in turn may have substituents selected from acyl, alkoxycarbonyl, alkenoxycarbonyl, aryl and hydroxy) and hydroxyl groups; and

R^{35} and R^{36} are independently H or alkyl of from 1 to 20 carbon atoms which alkyl groups, in turn may have substituents selected from acyl, alkoxycarbonyl, alkenoxycarbonyl, aryl and hydroxy, or R^{35} and R^{36} may be joined together to form an alkanediyl group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring.

40. A polymerisation process according to claim 39 in which the initiator is a compound of the formula IX



IX

wherein

R^{50} is a C_{2-6} alkanediyl, preferably straight chain, an alkoxyalkyl or an oligo (C_{2-3} oxy)- C_{2-3} alkyl;

X^2 is a halide;

each R^{31} is hydrogen; and

each R^{30} is a group COR^{34} in which R^{34} is a C_{1-6} alkoxy group.

41. A polymerisation process according to any of claims 38 to 40 which is carried out in the presence of a catalyst comprising a transition metal compound $M_t^{q+}X^3_q$, where:

M_t^{q+} may be selected from the group consisting of Cu^{1+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Ru^{2+}, Ru^{3+},Cr^{2+}, Cr^{3+}, Mo^{2+}, Mo^{3+}, W^{2+}, W^{3+}, Mn^{2+}, Mn^{3+}, Mn^{4+}, Rh^{3+}, Rh^{4+}, Re^{2+}, Re^{3+}, Co^{+}, Co^{2+}, Co^{3+}, V^{2+}, V^{3+}, Zn^{+}, Zn^{2+}, Ni^{2+}, Ni^{3+}, Au^{+}, Au^{2+}, Ag^{+} and Ag^{2+};

X^3 is selected from the group consisting of halogen, C_1-C_6-alkoxy, $(SO_4)_{½}$, $(PO_4)_{1/3}$, $(R^{37}PO_4)_{½}$, $(R^{37}{}_2PO_4)$, triflate, hexafluorophosphate, methanesulphonate, arylsulphonate, CN and $R^{38}CO_2$, where R^{37} is aryl or a straight or branched C_{1-20} alkyl and R^{38} is H or a straight or branched C_1-C_6

alkyl group which may be substituted from 1 to 5 times with a halogen; and

q is the formal charge on the metal ($0 \leq q \leq 7$); and

a ligand, selected from the group consisting of:

a) compounds of the formulas:

$$R^{39}\text{-}Z\text{-}R^{40} \quad \text{and}$$

$$R^{39}\text{-}Z\text{-}(R^{41}\text{-}Z)_m\text{-}R^{40}$$

where:

R^{39} and R^{40} are independently selected from the group consisting of H, C_1-C_{20} alkyl, aryl, heterocyclyl and C_1-C_6 alkoxy, C_1-C_4 dialkylamino, $C(=O)R^{42}$, $C(=O)NR^{43}_2$ and $A^7C(=O)R^{44}$, where A^7 may be NR^{45} or O; R^{42} is alkyl of from 1 to 20 carbon atoms, aryloxy or heterocyclyloxy; R^{43} is independently H or alkyl of from 1 to 20 carbon atoms or the two groups R^{43} may be joined together to form an alkanediyl group of from 2 to 5 carbon atoms, thus forming a 3- to 6-membered ring; R^{44} is H, straight or branched C_1-C_{20} alkyl or aryl and R^{45} is hydrogen, straight or branched $C_{1\text{-}20}$-alkyl or aryl; or R^{39} and R^{40} may be joined to form, together with Z, a saturated or unsaturated ring;

Z is O, S, NR^{46} or PR^{46}, where R^{46} is selected from the same group as R^{39} and R^{40}, and where Z is PR^{46}, R^{46} can also C_1-C_{20} alkoxy or Z may be a bond, CH_2 or a fused ring, where one or both of R^{39} and R^{40} is heterocyclyl,

each R^{41} is independently a divalent group selected from the group consisting of C_1-C_8 cycloalkanediyl, C_1-C_8 cycloalkenediyl, arenediyl and heterocyclylene where the covalent bonds to each Z are at vicinal positions or R^{41} may be joined to one or both of R^{39} and R^{40} to formulate a heterocyclic ring system; and

m is from 1 to 6;

b) CO;

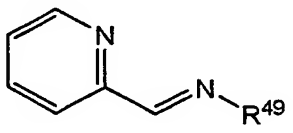
c) porphyrins and porphycenes, which may be substituted with from 1 to 6 halogen atoms, C_1-$_6$ alkyl groups, $C_{1\text{-}6}$-alkoxy groups, $C_{1\text{-}6}$

alkoxycarbonyl, aryl groups, heterocyclyl groups, and C_{1-6} alkyl groups further substituted with from 1 to 3 halogens;

d) compounds of the formula $R^{47}R^{48}C(C(=O)R^{49})_2$, where R^{49} is C_{1-20} alkyl, C_{1-20} alkoxy, aryloxy or heterocyclyloxy; and each of R^{47} and R^{48} is independently selected from the group consisting of H, halogen, C_{1-20} alkyl, aryl and heterocyclyl, or R^{47} and R^{48} may be joined to form a C_{1-8} cycloalkyl ring or a hydrogenated aromatic or heterocyclic ring, of which the ring atoms may be further substituted with 1 to 5 C_{1-6} alkyl groups, C_{1-6} alkoxy groups, halogen atoms, aryl groups, or combinations thereof; and

e) arenes and cyclopentadienyl ligands, where said cyclopentadienyl ligand may be substituted with from one to five methyl groups, or may be linked through an ethylene or propylene chain to a second cyclopentadienyl ligand.

42. A polymerisation process according to claim 41 in which the transition metal compound is CuBr, CuCl or RCl_2 and the ligand is bipyridine, or



where R^{49} is a suitable alkyl group, preferably C_{1-4} alkyl, triphenylphosphine or 1,1,4,7,10,10-hexamethyl-triethylene tetramine.